

# Paraelectric-to-ferroelectric crossover and electron dynamics from time-dependent Hartree-Fock calculations

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## Abstract

In recent years, researchers have discovered various excited states of electrons having an excited domain with a structural order different from the original one. We examine a dynamics of electron system and phonon system by using the time-dependent Hartree-Fock approximation. We examine time evolution with spin degree of freedom. We found a thermally excited paraelectric-to-ferroelectric crossover. The metastable state is spin pierls state. We also examine the Landau expansion of electron system at quarter-filled.

The paraelectric-to-ferroelectric crossover caused by electrons displacement is induced by an electron in an paraelectric insulating solid when it is excited by a electric external field.<sup>1</sup> The original concept of this relaxation assumes this crossover to be a microscopic phenomenon. The photo induced paraelectric-to-ferroelectric crossover can be called a photo-induced structural phase transition. In this paper, we examine the theoretical studies on photo induced problem. Photo-induced phase transitions have attracted much attention. This structural phase transition has often been described as a domino effect. It is highly nonlinear and cooperatives, in particular its time evolution is many body problem. The photo-irradiation a large energy is imported by the photo induced irradiation that is not accessible in thermal equilibrium. Thus even if photo-induced phase is one that is realized in such conventional method, the mechanism of the transition is not trivial at all. A large enhancement of dielectric constant by UV light irradiation is reported for the first time in quantum paraelectric family of perovskite oxides, such as  $\text{SrTiO}_3$  and  $\text{KTiO}_3$ , under a weak DC field.<sup>2</sup> The photo irradiation induce the paraelectric-to-ferroelectric crossover. as a function of temperature. Without photo irradiation, the dielectric property of these material is Quantum paraelectric. The DC electric field suppress the quantum fluctuation, which enhance the quantum domino catastrophes.

Photo-induced transitions have been studied in many method. Whether a deterministic or stochastic approach accurately describes the time evolution of electron system would depend on the time scale of observation. The recent study obviously needs to be described in a deterministic manner.<sup>?</sup> Their charge and lattice motion is calculated by using the time-dependent Schrodinger equation. In this paper, we study another itinerant electron system and phonon system. The present study differs from other studies, because we treat the electron transportation and many body interaction.

We examined the time evolution from the initial state to a stationary state of the electron system with random initial condition. During the evolution, the excited state changes into a metastable state. This method has advantage because in Ref.<sup>?</sup>, the spin degree of freedom can not be treated. Though, in our method, we can not treat the eigenstate in stead of that we can examine time evolution with spin degree of freedom. We also examine the Landau expansion of electron system at quater-filled.

The electron system and classical phonon system is described by a time dependent Hartree-Fock approximation. The classical phonon system is evaluated by leap-flog

method. We assume a that Hubbard model for thermal-fluctuation-induced paraelectric-to-ferroelectric crossover, as follows,

$$H_{el} = \sum_{i,\sigma} [h_i^F (c_{i,\sigma}^\dagger c_{i+1,\sigma} + h.c.) + h_{i,\sigma}^H n_{i,\sigma}], \quad (1)$$

$$h_i^F = t_0 + \alpha(u[i+1] - u[i]), h_{i,\sigma}^H = \frac{U}{2} n_{\bar{\sigma}}[i, t], \quad (2)$$

$$H_{ph} = \sum_i \frac{P_i^2}{2M} + k u[i]^2 \quad (3)$$

where  $t_0$  is tight binding hopping strength, and  $U$  is on-site Coulomb repulsion.  $c_{i,\sigma}^\dagger, c_{i,\sigma}$  is creation and annihilation operator at cite  $i$ , spin  $\sigma$ .  $H_{ph}$  phonon system Hamiltonian,  $P_i$  is momentum,  $M$  is mass  $k$  is stiffness,  $u[i]$  is distortion and  $\alpha$  is dimerization coupling constant between electron system and phonon system. We will examine the simple Hubbard model. While, the complexity of degrees of freedom are different, the universality should be the same, because the important quantity is the single band electron system. The time evolution is described by the correlation function,

$$g[i, j, t]^{\sigma\sigma'} = \langle c_{i,\sigma}^\dagger(t) c_{j,\sigma'}(t) \rangle. \quad (4)$$

The time evolution equations of a spin diagonal correlation function are

$$\begin{aligned} \frac{dg[i, j, t]^\sigma}{dt} = & -\frac{i}{\hbar} [h_i^F g[i+1, j, t]^\sigma + h_{i-1}^F g[i-1, j, t]^\sigma \\ & - h_{j-1}^F g[i, j-1, t]^\sigma - h_j^F g[i, j+1, t]^\sigma \\ & + h_{i,\sigma}^H g[i, j, t]^\sigma - h_{j,\sigma}^H g[i, j, t]^\sigma]. \end{aligned} \quad (5)$$

However, there is no eigenstate for this correlation function, in stead we can examine the time trace of system with random initial condition numerically. The equation corresponds to the random phase approximation. In present study, d-dimensional quantum field theory is equivalent to 2d classical field theory. During the time evolution, the initial excited state changes into the local ground state.

The Bloch-Wigner representation of the correlation function is,

$$g^\sigma[x, p] = \sum_m e^{imp} g^\sigma[k, l], \quad (6)$$

where  $x = k - l$ ,  $m = (k + l)/2$ . This representation is not positive definite, therefore probabilistic interpretation can not be applied.

First, we examine numerical solution. The numerical method comprises the Crank-Nicholson method<sup>4</sup> and the Gauss-Seigel Method. The time evolution of the Schrodinger equation is described by the unitary condition to 2nd-order approximation:

$$\exp(-iHt) \simeq \frac{1 + i\frac{1}{2}Ht}{1 - i\frac{1}{2}Ht}. \quad (7)$$

In present numerical study, we set the number of electrons to be 4 due to quarter-filled system. Let us examine the time dependence of the electron order parameter. CDW is the intensity of the alternative derivative of local charge density. AF is the intensity of the alternative derivative of local spin density. The order parameters are defined by

$$\begin{aligned} \text{CDW} &= \sum_{i,\sigma} (-1)^i (g[i+1, i+1, t]^\sigma + g[i-1, i-1, t]^\sigma \\ &\quad - 2g[i, i, t]^\sigma), \\ \text{AF} &= \sum_{i,\sigma} \sigma (-1)^i (g[i+1, i+1, t]^\sigma + g[i-1, i-1, t]^\sigma \\ &\quad - 2g[i, i, t]^\sigma). \end{aligned} \quad (8)$$

For the whole system the physical parameter is as follows,  $t_0 = 0.1, U = 0.5, k = 8, M = 500, \alpha = 0.1$  and unit of the time is normalized to the above parameters. The initial conditions are  $g[i, j, t]^\sigma = 0.25 + \beta * n$  where  $n$  is complex random value with absolute value 1 for all  $i, j, \sigma$ . and are  $\beta_{el} = 0.01$  or  $\beta_{el} = 0.1$ . This means the initial condition is a quarter-filled homogeneous state with off-diagonal coherence. For the Bloch-Wigner representation, after the time evolution, the momentum distribution of the charges is oscillating and has domain in real space. The strengths of higher moment are weak. This result is similar to the Haldane conjectures.

The CDW state order parameter is  $4k_F$  CDW order parameter.<sup>3</sup> The AF state order parameter is  $4k_F$  ant ferromagnetic order parameter. Thus, the  $4k_F$  CDW is quantum paraelectric order parameter, The dimerization enhance the  $4k_F$  CDW state. The AF state order parameter represent spin pierls instability. For strong noise, AF state order parameter decreases and CDW state order parameter increases with time. The time trace of the two order parameters become in phase. The time trace of order parameters shows the phase of two order parameters depends on noise strengths. Exactly the final stage, CDW state order parameter is positive for the figs.1 and 2, and AF state order parameter phase is become

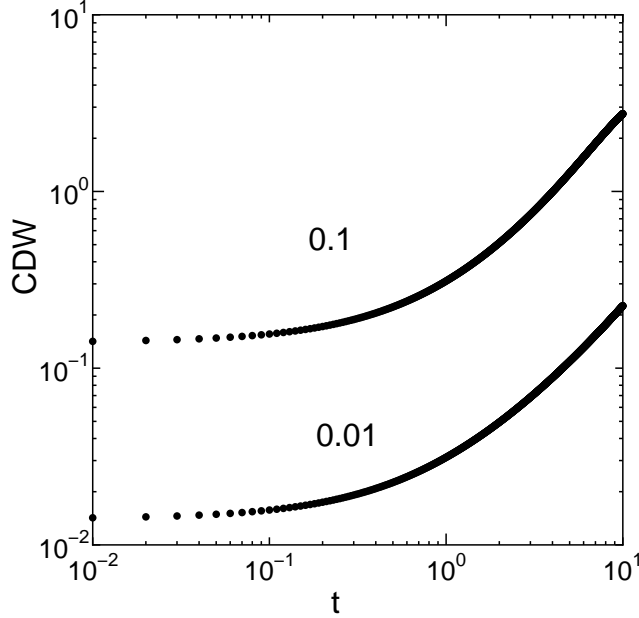


FIG. 1: Time dependence of electron order parameter.  $\beta_{el} = 0.01$  and  $0.1$  no phonon

negative for figs.3 and 4, when strong randomness. This phase locking due to the quasi-one-dimensional interchain coupling is assumed. The figs.1 and 2 is ground state and figs. 3 and 4 is metastable state. The strong randomness leads to metastable state.

Due to complex initial condition, the transition from metastable state to the order ground state occurs. When  $\beta=0.01$ , the AF order parameter increases, this indicates the Wigner crystal insulator. When  $\beta=0.1$ , the AF order parameter become negative, the cross over to spin piers state (ferroelectric) occurs. An experiment has shown the existence of a photo-induced paraelectric-to-ferroelectric phase crossover.<sup>2</sup> Thus, we have examine this crossover from the viewpoint of non-equilibrium condensed matter theory by using a Hubbard model Hamiltonian in view point of time dependent Hartree-Fock calculation. The transverse photo effect behaves as thermal fluctuation. The thermal fluctuation creates a non-equilibrium state with finite order parameter and settled random initial condition. The complex random initial condition correspond to the excited phonon with imaginary self energy. Thus the emission and absorption of phonon system by electric external field is essential for photo-induced effect. An external electric field leads to the catastrophe for the domino system. The paraelectric comes from quantum fluctuations between dominoes. This just the thermal

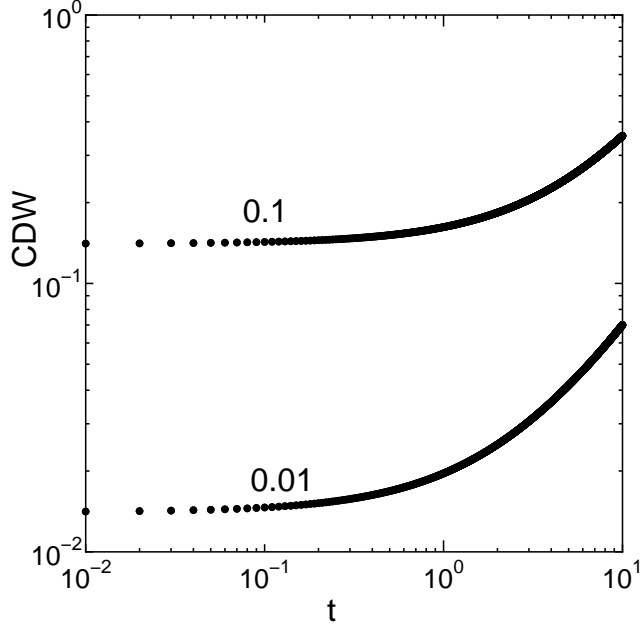


FIG. 2: Time dependence of electron order parameter.  $\beta_{el} = 0.01$  and  $0.1$  aco phonon

fluctuation induced quantum domino effect. The displacement of the dipole is suppressed because of the repulsion between the dipole moment.

Next, we divide system A and B sub lattice. The Bloch-Wigner representation has to generate effective energy. First, the property of Liouville operator is given by,

$$\frac{dg^\sigma[x, p]}{dt} = \frac{1}{\hbar} \{W_\sigma, g^\sigma[x, p]\}, \quad (9)$$

$$\{A, B\} = \frac{\partial A}{\partial x} \frac{\partial B}{\partial p} - \frac{\partial A}{\partial p} \frac{\partial B}{\partial x}, \quad (10)$$

$$W_\sigma = -2t_0 \cos p + h_x^H. \quad (11)$$

The obtained effective energy is derived Moyal-Krammer formulation, as follows,

$$E_{eff} = \sum_{\sigma, \alpha} W_{\sigma, \alpha} n_{\sigma, \alpha}. \quad (12)$$

where  $\alpha$  and A or B. Present representation of effective energy

$$\begin{aligned} E_{eff} = & \sum_{\sigma} \left( \frac{U}{2} \langle n_{\sigma}^A \rangle - 2t_0 \cos p \right) \langle n_{\sigma}^A \rangle . \\ & \sum_{\sigma} \left( \frac{U}{2} \langle n_{\sigma}^B \rangle - 2t_0 \cos p \right) \langle n_{\sigma}^B \rangle . \end{aligned} \quad (13)$$

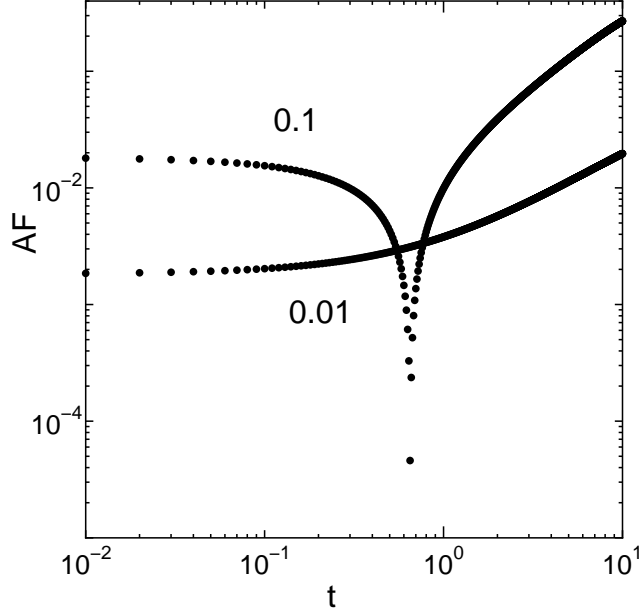


FIG. 3: Time dependence of spin order parameter.  $\beta_{el} = 0.01$  and  $0.1$  no phonon

where we neglect the fock term. Next we assume the system is Wigner crystal. The charge density is  $4k_F$  and spin density is non magnetic.

$$\langle n_\sigma^A \rangle = \frac{1 + \Delta}{4}, \langle n_\sigma^B \rangle = \frac{1 - \Delta}{4}. \quad (14)$$

Thus, effective energy is given by

$$E_{eff} = U \frac{1 - \Delta^2}{8} - 2t_0 \cos p \quad (15)$$

Then we examine Landau expansion which obtained by free energy,

$$F_{eff} = E_{eff}|_{\Delta=0} + \frac{\delta E_{eff}}{\delta \Delta} \Delta + \frac{1}{2} \frac{\delta^2 E_{eff}}{\delta \Delta^2} \Delta^2 + k_B T \int dx dp [f \ln f + (1 - f) \ln(1 - f)]. \quad (16)$$

The last part of the above equation is approximated as follows,

$$\begin{aligned} & k_B T \int dp dx [\ln \frac{f}{1-f}]|_{\Delta=0} \frac{\delta f}{\delta \Delta}|_{\Delta=0} \Delta \\ & + k_B T \int dp dx [\frac{1}{f} + \frac{1}{1-f}]|_{\Delta=0} (\frac{\delta f}{\delta \Delta})^2|_{\Delta=0} \frac{\Delta^2}{2} \\ & + k_B T \int dp dx [\ln \frac{f}{1-f}]|_{\Delta=0} \frac{\delta^2 f}{\delta \Delta^2}|_{\Delta=0} \frac{\Delta^2}{2} \end{aligned}$$

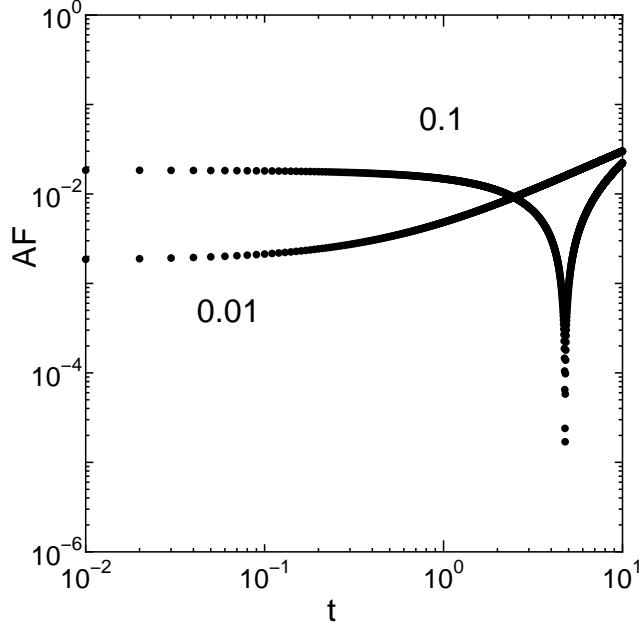


FIG. 4: Time dependence of spin order parameter.  $\beta_{el} = 0.01$  and  $0.1$  aco phonon

$$\begin{aligned}
& + k_B T \int dp dx \left[ -\frac{1}{f^2} + \frac{1}{(1-f)^2} \right]_{\Delta=0} \left( \frac{\delta f}{\delta \Delta} \right)^3 \Big|_{\Delta=0} \frac{\Delta^3}{3!} \\
& + k_B T \int dp dx \left[ \frac{1}{f} + \frac{1}{1-f} \right]_{\Delta=0} \frac{\partial}{\partial \Delta} \Big|_{\Delta=0} \left( \frac{\partial f}{\partial \Delta} \right)^2 \Big|_{\Delta=0} \frac{\Delta^3}{3!} \\
& + k_B T \int dx dp \left[ \frac{2}{f^3} + \frac{2}{(1-f)^3} \right]_{\Delta=0} \left( \frac{\partial f}{\partial \Delta} \right)^4 \Big|_{\Delta=0} \frac{\Delta^4}{4!} \\
& + k_B T \int dp dx \left[ -\frac{1}{f^2} + \frac{1}{(1-f)^2} \right]_{\Delta=0} \frac{\partial^4 f}{\partial \Delta^4} \Big|_{\Delta=0} \frac{\Delta^4}{4!} \\
& + k_B T \int dp dx \left[ -\frac{1}{f} + \frac{1}{(1-f)} \right]_{\Delta=0} \frac{\partial^2}{\partial \Delta^2} \Big|_{\Delta=0} \left( \frac{\partial f}{\partial \Delta} \right)^2 \Big|_{\Delta=0} \frac{\Delta^4}{4!}.
\end{aligned} \tag{17}$$

In summary 2-nd order expansion is

$$A_2 = \frac{U}{4} \left( 1 - \frac{U}{4} \rho(e_F) \right), \tag{18}$$

where  $\rho(e_F)$  is density of state of electron. The 3-rd order coefficient is

$$A_3 = \frac{k_B T \rho(e_F) U}{4}. \tag{19}$$

The expression of 4-th order is given as

$$A_4 = \frac{k_B T \rho(e_F) U}{4}. \tag{20}$$



Thus, this system is asymmetric double well system. However, due to the low dimensional fluctuation there are no phase transition.

In summary, we found a thermally excited paraelectric-to-ferroelectric crossover. We examined time evolution of electron system with spin degree of freedom and phonon system. The quantum noise corresponds phonon excited by the electric external field. The imaginably random initial condition corresponds to emission and absorption of excited phonon by electric external field. The stronger randomness leads to metastable spin pierls state. The metastable state is unstable non-equilibrium state. This is ferroelectric state. We suggest such a non-equilibrium effect is necessary to photo induced effects. We also examine the Landau expansion of electron system at quarter-filled.

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